Effect of Sulfur Recovery Requirements on Optimization of Integrated Sweetening, Sulfur Recovery, and Tailgas Cleanup Units

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ABSTRACT

Emphasis on environment concerns has pushed sulfur emissions to the fore-front. Present three stage Claus plants cannot reach the sulfur recovery requirement for small gas processing plants, therefore some form of special tail gas cleanup unit is required. Several processes yield higher recoveries than the three stage Claus unit but this paper is directed to an integrated system with a primary amine unit, a Claus unit, and a tail gas clean up unit. The overall sulfur recovery is in excess of 99.8%.

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INTRODUCTION

With the increasing environmental concerns, sulfur recovery has become one of the leading issues in emissions reduction. As stated by Blevins, the sulfur recovery requirements range from 97.5% to 99.8+% for gas processing and refining facilities processing 10 LT/d and greater.[1] The higher recovery of 99.8+% is required for most facilities with 20 LT/d and higher. Since most three stage Claus plants cannot achieve recoveries significantly greater than 96%, some form of tailgas cleanup or special processing capability will be required for facilities processing 10 LT/d and greater.

The technologies available to yield recoveries higher than the three stage Claus unit include Cold Bed Adsorption (CBA), LoCat®, SCOT®, Stretford®, Superclaus®, and oxygen enrichment such as the COPE® process. In the CBA, LoCat, and oxygen enrichment processes, the higher recoveries may be achieved without a tailgas cleanup unit (TGCU). The Stretford process and Superclaus may be used as either the primary sulfur recovery process or the TGCU. The SCOT type process is the oldest and most common type of TGCU. It converts the sulfur in the tailgas back to hydrogen sulfide (H_2S) and then scrubs the H_2S in a low pressure amine sweetening unit and recycles the absorbed acid gases to the Claus unit. In the present paper, the emphasis is on an integrated system consisting of a primary amine unit, Claus sulfur recovery unit, and TGCU. This type of system is usually capable of achieving sulfur recoveries greater than 99.8%.

To examine the effect of sulfur recovery requirements on the optimization of integrated sweetening, sulfur recovery and TGCU's, a process simulation program called TSWEET® (Bryan Research & Engineering) was used.[2] TSWEET can simulate the entire system including sweetening, sulfur recovery, and TGCU in a single run permitting convenient optimization of the entire complex. The amine sweetening capabilities include monoethanol amine (MEA), diglycol amine (DGA), diethanol amine (DEA), methyldiethanol amine (MDEA), and mixtures of these amines while the sulfur recovery simulation capabilities include Claus, CBA, Selectox, Superclaus, and oxygen enrichment.

OPERATING CONDITIONS AND PARAMETERS AFFECTING SYSTEM PERFORMANCE

To better understand the effect of sulfur recovery requirements on the optimization of an integrated sweetening, sulfur recovery, and TGCU system, a brief discussion of several of the operating conditions and parameters which have a significant impact on the size, costs and performance of the system is presented. These will be discussed on a unit by unit basis.

Primary Sweetening Unit

The two major factors in the primary sweetening unit affecting the performance of the integrated system are the CO_2 and hydrocarbon pickup.

CO_2 pIckup

The CO_2 in the acid gas from the sweetening unit affects the system in two ways. Obviously, the size of the sweetening unit varies directly with the CO_2 pickup. In addition, since it is a diluent in the sulfur plant, it reduces the sulfur conversion to some degree. This influence is magnified by the fact that the TGCU absorber picks up part of the CO_2 in the tailgas and recycles it back through the system. Thus, the CO_2 pickup also leads to a larger sulfur plant and TGCU. The only possible relief to this problem, if specifications permit, is to slip more CO_2 in the overhead of the main absorber by switching to a more selective amine or by changing the operating conditions in the absorber to achieve greater selectivity.

Hydrocarbon pickup

Higher absorber pressures and heavier hydrocarbons tend to increase the net amount of hydrocarbon in the rich amine. Due to the combined effect, these hydrocarbons influence the system performance efficiently. In the furnace, the hydrocarbons are converted to mostly CO_2 with its attendant problems previously discussed, and to H_2O which drives the sulfur reaction in the wrong direction. In addition, the hydrocarbons are known to affect the amount of COS and CS_2 formed in the furnace (Fischer, Parnell, and Luinstra and d'Haene).[3,6,5]

The only convenient means to reduce the hydrocarbon problem is to add a low pressure flash tank on the rich amine stream.

Claus Sulfur Plant

Due to high temperatures involved, the reactivity of the components and the associated sampling and analysis problems, the extent of formation or destruction of H_2, CO, COS, NH_3, and CS_2 in the furnace and their subsequent degree of reaction in the waste heat boiler has been very difficult to measure. This topic has been widely discussed in the literature.[3,5,6]

H_2 and CO formation and reaction

Significant amounts of H_2 and CO are formed in the acid gas burner depending on the acid gas composition and flame temperature. Some disagreement exists over the degree to which the H_2 and CO participate in the reactions as the gases are cooled in the waste heat boiler and in the reactions in the catalyst beds. The most common beliefs are that the reactions occur to only a moderate degree in the waste heat boiler. Based on data from a large number of plants the degree of reaction is best represented by quenching all of the reactions in the waste heat boiler at 100^oF below the flame temperature with a minimum quench temperature of 2000^oF. Most experts believe that there is no reaction in the Claus beds by either H_2 or CO.

COS and CS_2 Formation and Reaction

COS is believed to be formed in the furnace from the reaction of carbon monoxide with sulfur (Kerr and Paskall) while CS_2 is believed to be formed by the reaction of hydrocarbons directly with elemental sulfur (Luinstra and d'Haene).[4,5] Due to the sampling and analysis problems, the amount of COS and CS_2 formed is most easily described in terms of the net formation in the furnace and waste heat boiler. The most convenient procedure is to assume that the net amount is formed in the furnace and that none of it reacts in the cooling process in the waste heat boiler.

COS and CS_2 are difficult to react in the catalyst beds and require a special catalyst with its associated operating conditions. These conditions (high temperatures) will reduce the effectiveness of the first bed in converting H_2S and SO_2, but if the COS and CS_2 are not converted in the sulfur plant, they will be reduced to H_2S in the TGCU, thus increasing the size of both the TGCU and sulfur plant.

Configuration

The reheat configurations which are used in sulfur recovery units include indirect, hot-gas bypass, and in-line burner. Since the other two involve bypassing one or more of the beds with part of the H_2S, the indirect reheat method produces the highest recoveries.

Tailgas Cleanup Unit

The most important operating parameter of interest in the TGCU is CO_2 rejection in the TGCU absorber.

CO_2 rejection in TGCU absorber

Obviously, the real key to TGCU performance is the ability to reject CO_2 in the tailgas absorber. In most cases, this feature has a moderate effect on the size and effectiveness of the sulfur plant and a profound effect on the TGCU absorber. All of the design considerations to increase selectivity must be fully optimized including amine selection, liquid residence times on the absorber trays, solution loading, and absorber operating temperature.

ANALYSIS AND DISCUSSION OF RESULTS

A wide range of operating conditions was explored to determine the effect of the sulfur recovery requirements on the system performance. A base case (Table I) was selected for study that had a 0.5 H_2S/CO_2 ratio in the feed gas to the main sweetening unit to examine a range of scenarios. Since this base will, in many situations, yield a rather poor quality feed to the sulfur recovery unit, the analysis will include many of the worse case type conditions.

Table I.

Operating conditions for example sulfur recovery unit, base case

Composition of gas streams	Sour gas Mol %	Acid gas Mol %	Claus tailgas Mol %
Nitrogen	0.0	0.0	33.29

Hydrogen	0.0	0.0	0.39
Hydrogen Sulfide	1.0	30.5	0.19
Sulfur Dioxide	0.0	0.0	0.09
Carbonyl sulfide	0.0	0.0	0.04
Carbon monoxide	0.0	0.0	0.95
Carbon Dioxide	2.0	60.82	44.39
Water	Saturated	6.33	20.66
Methane	89.0	2.12	0.0
Ethane	5.0	0.15	0.0
Propane	2.0	0.04	0.0
Butane	1.0	0.04	0.0
Volume, MMscfd	30	0.982	2.14
Temperature, ^oF	70	120	280
Pressure, psia	430	26.5	20.7

Amine unit operating conditions

Amine	DEA
Concentration	30 % wt
Rich Loading	0.3 mol/mol
Circulation	250 gpm
Absorber ideal stages	7
Stripper ideal stages	10
Stripper steam rate	1 lb/gal
Trim cooler temperature	120^oF

Claus unit operating conditions

Number of beds	3
Reheat	Indirect
Condenser 1, temperature	350^oF
Condenser 2, temperature	320^oF
Condenser 3, temperature	320^oF
Condenser 4, temperature	280^oF
Bed 1, inlet temperature	535^oF
Bed 2, inlet temperature	405^oF
Bed 3, inlet temperature	370^oF

TGCU operating conditions

TGCU reactor temperature	700^oF
Spray tower exit temperature	124^oF
TGCU absorber ideal stages	5
TGCU stripper ideal stages	10
TGCU stripper steam rate	1 lb/gal

The analysis was designed to obtain the maximum possible conversion. All beds were reheated indirectly unless otherwise noted. The bed operating temperatures were as cool as practical without falling into either the sub dewpoint or below COS and CS_2 conversion temperature in the first bed. The condensers were also operated as cool as practical. The conversion efficiencies for the beds were set to 100%. As the catalysts in the beds degrade and sulfur condenser tubes foul, plant performance will decline by amounts which are determined by bed size and degree of fouling.

For most cases, the volumetric flow rate from the last sulfur condenser, the solution circulation rate in the absorber, and the overall sulfur recovery were used as indicators of plant size and performance.

The effect of the CO_2 pickup in the main amine unit was examined by running the base case with complete acid gas pickup and then with varying degrees of CO_2 slippage to the sales gas. As can be seen in Figure 1, the gas flow rate through the catalyst bed starts to increase sharply at H_2S/CO_2 ratios below about 1.0. If the operating parameters in the sulfur plant and TGCU are maintained constant, the sulfur recovery drops very rapidly at H_2S/CO_2 ratios below 1.0 as shown in Figure 2. The hydrocarbon pickup in the amine unit has little affect on the sulfur recovery up to about 1.5% propane equivalent in the feed gas to sulfur recovery unit. If the sour gas is at high pressure, a flash tank on the rich amine stream will significantly reduce the dissolved hydrocarbons.

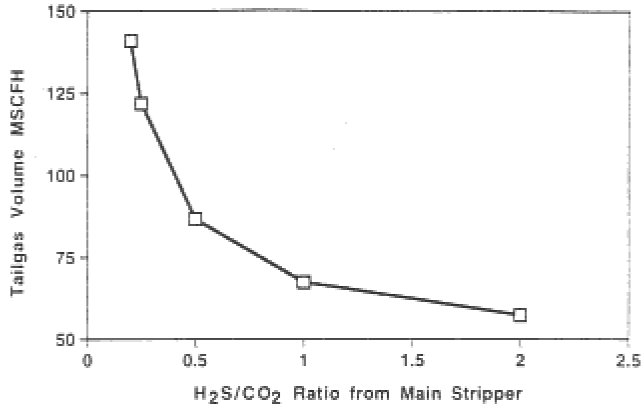


Figure 1. Effect of H2S/CO2 ratio in feed to sulfur unit on size of sulfur unit.

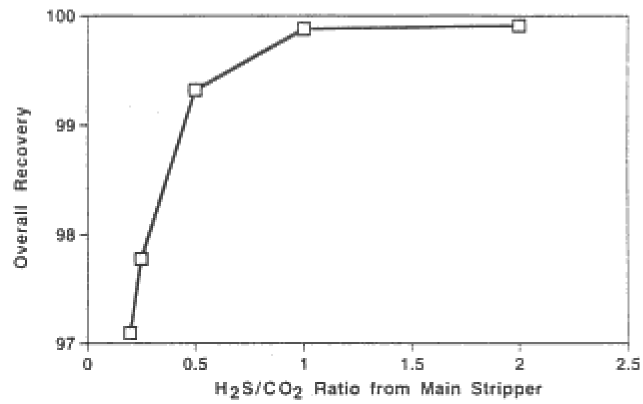


Figure 2. Effect of H2S/CO2 ratio in feed to sulfur unit on overall recover with a TGCU.

In the sulfur recovery unit, the amount of H_2 and CO formed and carried through the unit primarily affects the distribution of the sulfur between the beds and has little affect on the per pass recovery. The amount of COS and CS_2 formed in the burner has little affect on the per pass recovery as long as the proper decomposition catalyst is used in the first bed with the proper operating conditions.

A performance comparison between two and three bed sulfur units with indirect reheat and three bed with in-line burners is shown in Figure 3. The per pass recovery under ideal conditions ranges from about 99.5% to nearly 98% with the three bed with in-line burner being almost midway between the two and three bed with indirect reheat cases. This figure also shows that increased amine circulation rate in the TGCU with its resultant increase in CO_2 recycled has little affect on the per pass recovery in the sulfur unit.

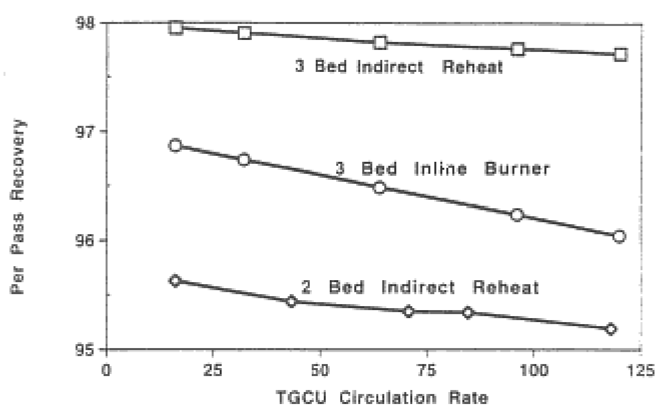


Figure 3. Effect of plant configuration and TGCU circulation on per pass recovery.

In the hydrogenation step of the TGCU, care must be taken to ensure that excess reducing gas does not result in NH_3 production in the TGCU reactor. If NH_3 is formed, it will pull acid gases into the water in the quench tower. If NH_3 reaches the TGCU absorber, it will pull CO_2 into the solution and greatly reduce the selectivity. The water quench tower serves to remove excess water from the acid gas stream and must be operated below about 120^{o}F to prevent water accumulation in the TGCU amine unit as shown in Figure 4. Higher temperatures also reduce the ability of the amine in the TGCU to slip CO_2.

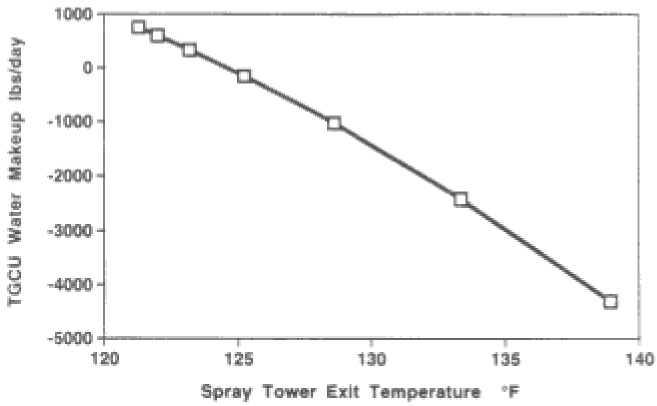


Figure 4. Effect of quench temperature on TGCU water makeup.

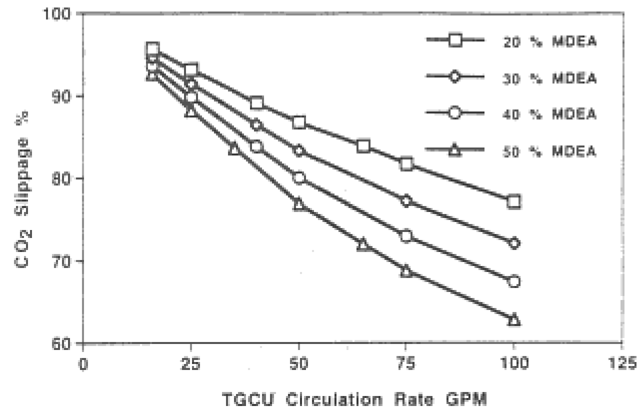


Figure 5. Effect of TGCU circulation rate and wt % amine on CO2 slippage.

In the TGCU amine unit, the overwhelming performance factor is the ability to reject or slip CO_2 while absorbing the necessary H_2S. The major factors affecting the CO_2 slippage in the absorber are the number of trays, the liquid residence time on the trays, the concentration of the amine, and the circulation rate. In most cases, 12 to 15 actual trays are used which is equivalent to four or five ideal stages. The liquid residence time should be kept as low as possible and usually in the range of 1.5 to 2.0 seconds. As shown in Figure 5, the amine concentration and circulation rate have a large effect on the CO_2 slippage. The lowest circulation rate possible with a 20 % wt methyldiethanol amine (MDEA) solution gives the best CO_2 slippage. The dramatic effect of the amine concentration on the CO_2 slippage can be clearly seen in Figure 6 for a given circulation rate of 75gpm. As can be seen in Figure 7, the size of the sulfur recovery unit is strongly affected by CO_2 slippage in the TGCU.

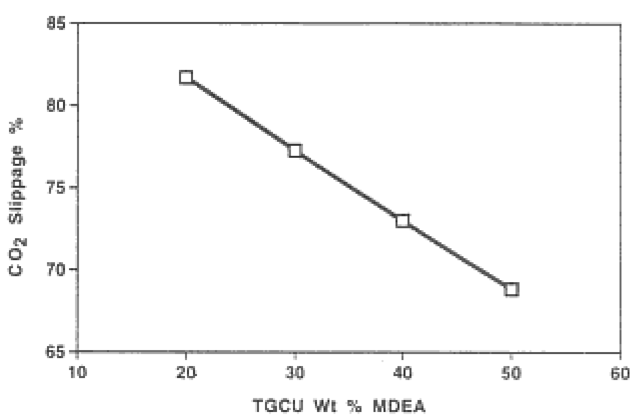


Figure 6. Effect of wt % amine on CO2 slippage in TGCU at 75 gpm.

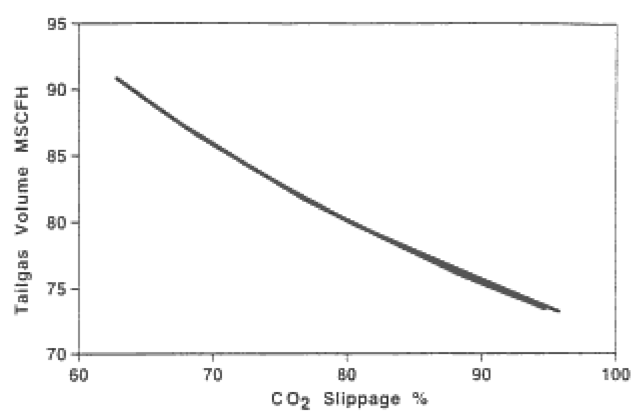
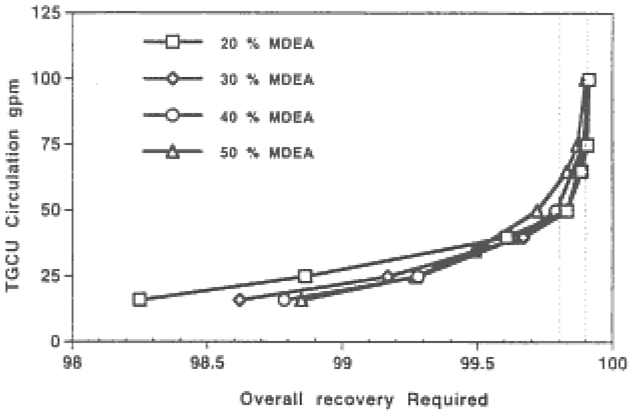


Figure 7. Effect of CO2 slippage in TGCU on sulfur plant size.

For the base case of a H_2S/CO_2 ratio of 0.5 in the Claus plant feed, the influence of the required overall sulfur recovery on the TGCU amine circulation rate can be observed in Figure 8. This shows that the size of the TGCU rises sharply with required recovery above about 99.8%. As discussed previously, the higher circulation rates lead to much lower CO_2 slippages. The increased CO_2 recycled has a large effect on the size of the sulfur recovery unit as shown in Figure 9. For better quality feeds to the sulfur plants, higher recoveries can be reasonably achieved since the H_2S in the tailgas can be removed before the CO_2 absorption overwhelms the plant.



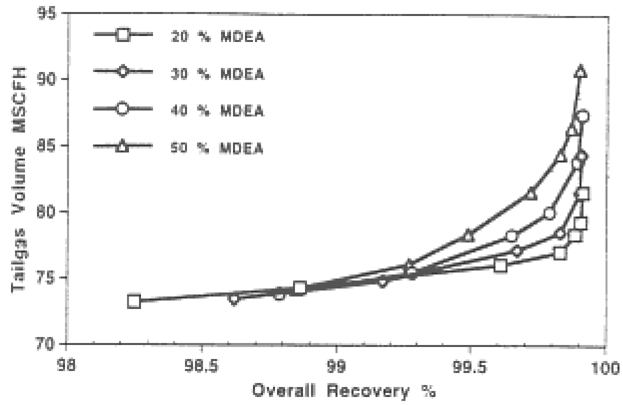


Figure 8. Impact of sulfur recovery requirements on TGCU circulation rate. Figure 9. Effect of sulfur recovery requirements on plant size (with TGCU).

CONCLUSION

Integrated gas sweetening, sulfur recovery, and tailgas cleanup units (TGCU) were examined using a process simulation program to determine the influence of sulfur recovery requirements on the performance of the system. A base case with an H_2S/CO_2 ratio of 0.5 in the feed gas was selected to represent a "worst-case" scenario. For the assortment of cases considered, the results showed that the importance of many operating parameters was very dependent on the level of sulfur recovery required.

For facilities with less than 10 LT/d of sulfur and recovery requirements below 97%, all of the fine adjustments in the sulfur plants including the catalyst, type of reheat, and better controls should be pursued fully to eliminate the requirement for a TGCU. However, once the TGCU is added in the larger plants, the fine adjustments in the sulfur plant become less important. The major factors become the CO_2 slippage in the main amine unit (i.e. quality of Claus plant feed) and in the TGCU absorber. For cases where the H_2S/CO_2 ratio in the feed gas to the main sweetening unit is less than about 1.0, the CO_2 must be eliminated from the system by slippage in the main absorber or the TGCU absorber. For poor quality feeds to the sulfur recovery unit, recoveries of about 99.8% are close to the maximum achievable with TGCU technology. If the recovery requirements rise above the range 99.8% to 99.9%, other technologies for treating the tailgas such as Stretford or direct oxidation processes will be necessary, especially for the poorer quality feeds to the sulfur recovery units.

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